PHYSICAL REVIEW B **69**, 020409(R) (2004)

Orbital dimerization in $NaTiSi_2O_6$: An orbital analogue of the spin-Peierls phase transition

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(Received 15 September 2003; published 26 January 2004)

We measure the Raman scattering spectra of $NaTiSi_2O_6$, analyze the vibrational properties, and study the origin of the phase transition in this compound. In this quasi-one-dimensional $S=1/2$ system we observe anomalous high-temperature phonon broadenings, and large changes of the phonon energies and line-widths across the phase transition temperature of 210 K. These results, combined with theoretical considerations, indicate that the phonon anomalies originate from an orbital order-disorder type of phase transition. We find that the high temperature dynamical Jahn-Teller phase of $NaTiSi_2O_6$ exhibits a spontaneous breaking of translational symmetry into a dimerized, Jahn-Teller distorted, orbital ordered state under the formation of spin valence bonds.

DOI: 10.1103/PhysRevB.69.020409 PACS number(s): 75.30.Et, 75.50.Ee, 78.30.−j, 71.27.+a

Electrons in strongly correlated transition-metal compounds can be regarded as having separate spin, charge, and orbital degrees of freedom. It is the interplay between these, combined with their coupling to the lattice, that gives rise to a wealth of possible spin, charge, and orbital orderings, as observed for instance in many colossal magneto resistance manganites,[1] cuprates,[2] titanates [e.g., $LaTiO_3$ (Ref. 3)] and vanadates [e.g., V_2O_3 (Ref. 4) and $LiVO_2$ (Ref. 5)]. Systems with orbital degeneracy are particularly interesting because orbitals couple to the lattice via the cooperative Jahn-Teller (JT) effect, on the one hand, and via superexchange interactions to the electronic spin on the other hand.[2] Therefore, at an orbital ordering phase transition, the magnetic susceptibility and phonon properties will be affected at the same time. Experimentally, however, such an interrelation is seldom found: in general the dominant JT orbital-lattice coupling obscures the more subtle effects due to the superexchange.

Recently, a new type of magnetic phase transition is observed in $NaTiSi_2O_6$.[6] The magnetic susceptibility of $NaTiSi_2O_6$ (Ref. 6) sharply decreases below 210 K, indicating a transition to a nonmagnetic, spin-singlet state, with signs of a opening of the spin-gap, in contrast to previous studies of the pyroxene family, which showed that almost all compounds in this class exhibit long-range antiferromagnetic (AF) ordering at low temperatures.[6–9] $NaTiSi_2O_6$ belongs to the pyroxene family which consists of large group of compounds with a chemical formula AMB_2O_6; $A=$alkali-metal, $M=$transition-metal, and $B=$Si, Ge. Their structure[10] consists of isolated quasi one-dimensional chains of edge-sharing MO_6 octahedra, linked together by the corner-sharing BO_4 tetrahedra; see Fig. 1(a). The magnetic moments come from the M ions, with a value that depends on the ionic state (for example: Ti^{3+} corresponds to $S=1/2$, V^{3+} to $S=1$, Cr^{3+} to $S=3/2$, and so on). Because of the peculiar crystal structure of AMB_2O_6, the magnetic interactions are expected to be dominant and homogeneous (all M ions are in equivalent crystallographic positions) within the chains, see Fig. 1(b), so the sodium-silicon system with titanium ($S=1/2$) could be a prime candidate to show a spin-Peierls (SP) phase transition. Indeed, the behavior of the magnetic instability at T=210 K could, in principle, be of the SP type. This is further supported by an x-ray study,[11] which shows existence of a large alternation of the Ti-Ti distance at temperatures below T_c. But already the high-temperature magnetic susceptibility data does not support such a SP scenario, since the phase transition occurs at a temperature that is higher then the maximum point of the

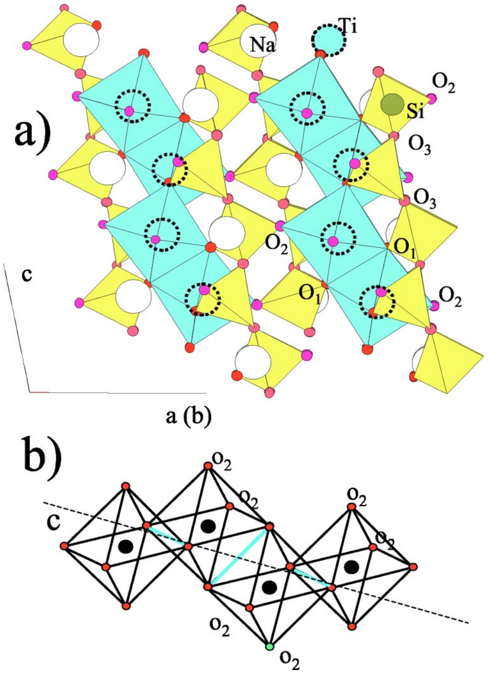

FIG. 1. (Color online) (a) Crystal structure of $NaTiSi_2O_6$. (b) A fragment of the crystal structure showing the geometry of the TiO_6 chain.

Bonner-Fisher curve,[12] which implies that the transition cannot solely be driven by magnetic fluctuations.[6] It is important to note that $NaTiSi_2O_6$ is a system with *active* t_{2g} orbitals so, besides anisotropy, the electronic interactions in this compound are expected to be governed by orbital degeneracy and/or JT effects. However, the structure of TiO_6 single octahedra deviate from full octahedral symmetry, which in general removes the threefold degeneracy of the t_{2g} state due to crystal field effect. As anticipated by Isobe *et al.*,[6] if this effect is combined with the specific chain geometry [connecting edges of the octahedra do not lie in the same plane; see Fig. 1(b)], this structure should be predisposed to orbital dimerization.

In this Communication, we further analyze the physical properties of $NaTiSi_2O_6$, and we answer the following questions: Why are the magnetic/physical properties of $NaTiSi_2O_6$ different from other isostructural pyroxenes, and what is the origin of the phase transition in this compound? We report a Raman scattering study of $NaTiSi_2O_6$ from which we conclude that orbital degrees of freedom indeed play a decisive role in the physical properties of this compound. We argue that $NaTiSi_2O_6$ undergoes an orbital order phase transition at $T_{OO} = 210$ K which can be regarded as an orbital analogue of the SP phase transition. We find that the dramatic drop of the magnetic susceptibility below T_{OO} is accompanied by a structural change, just as one would expect for a canonical orbital ordering transition. At high temperatures the fluctuations of the orbital degrees of freedom lead to a dynamic Jahn-Teller phase with anomalous phonon broadening and remnant AF spin fluctuations. These results, combined with the microscopic orbital-spin model that we derive, suggest that the quasi one-dimensional dynamical Jahn-Teller phase of $NaTiSi_2O_6$ exhibits a spontaneous breaking of the translational symmetry into a dimerized orbital ordered state with a spin gap due to the formation of spin valence bonds.

This Communication is organized as follows: first we present the Raman spectra and underline important observations, then we discuss the general electronic structure of pyroxenes and derive a microscopic model. Finally, we demonstrate that all observed effects (including the susceptibility data) can be accounted by our model.

High-quality powder samples of $NaTiSi_2O_6$ are prepared by a solid-state reaction of mixtures with an appropriate molar ratio of $Na_2TiSi_4O_{11}$, Ti and TiO_2. Details of the sample preparation are published elsewhere.[6] Raman spectra are measured in the backscattering configuration, using the 514.5- and 488-nm lines, of an Ar-ion laser, a micro-Raman system with a DILOR triple monochromator, and a liquid nitrogen cooled charge-coupled device detector. The pyroxenes crystallize in a monoclinic unit cell with the space group $C2/c$.[10] The unit cell consists of four formula units ($Z=4$) with 40 atoms in all. The site symmetry of Na, M, Si, O_1, O_2, and O_3 atoms are $(4e)$, $(4e)$, $(8f)$, $(8f)$, $(8f)$, and $(8f)$, respectively. Thus, the factor-group-analysis (FGA) yields

$$\Gamma^{opt.}_{NaMSi_2O_6} = 14A_g(xx,yy,zz,xz) + 16B_g(xy,yz) + 13A_u(\mathbf{E}||\mathbf{y}) + 14B_u(\mathbf{E}||\mathbf{x},\mathbf{E}||\mathbf{z}).$$

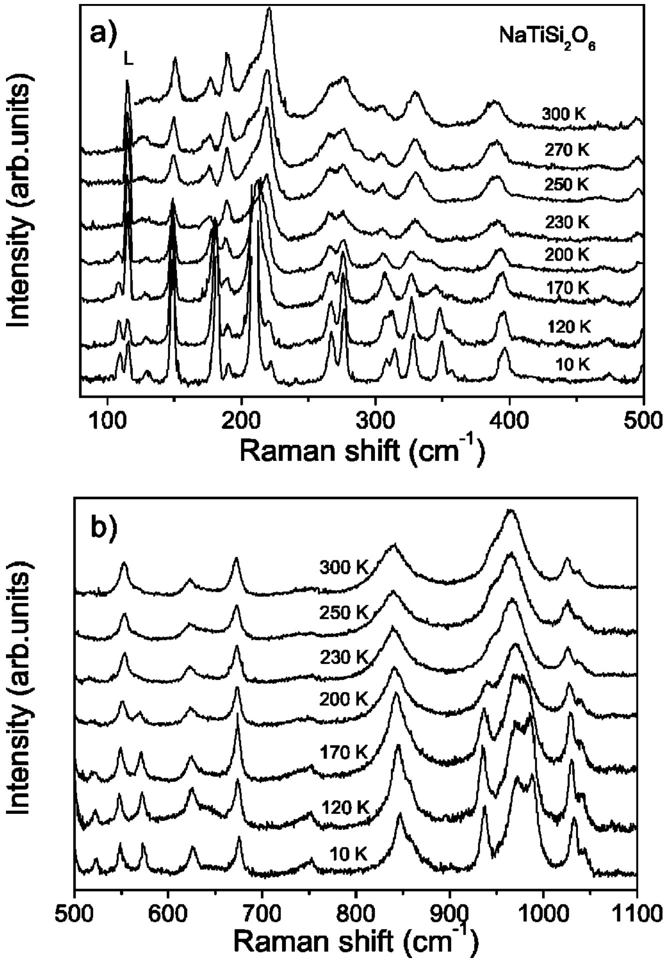

FIG. 2. Temperature dependence of the (a) low frequency and (b) high frequency Raman spectra in $NaTiSi_2O_6$.

The unpolarized Raman spectra of $NaTiSi_2O_6$ are shown in Fig. 2. We find of the order of (but fewer than) 30 phonon modes as predicted by the FGA which can be roughly grouped into two energy regions. The modes in the spectral range below 500 cm^{-1} originate from the bond bending vibrations, whereas the higher frequency modes originate from the stretching vibrations. By lowering the temperature we find a dramatic change in the phonon Raman spectra of $NaTiSi_2O_6$ around 210 K; see Figs. 2 and 3. First, even though we made unpolarized measurements, we observe the symmetry change of phonon excitations below T_c on the basis of their anti-crossing behavior. Namely, the modes at 221 and 209 cm^{-1} shift towards each other above T_c and away from each other below T_c (the anticrossing behavior) [see Fig. 3(b)], which indicates that these two modes belong to the same symmetry class below T_c (the interaction switches on at T_c so two modes with the same symmetry can not have the same energy). A similar effect is observed for other such pairs of modes (pairs are also found at about 180 and 190 cm^{-1} and at about 550 and 567 cm^{-1}) in the spectra, which suggests that in the low-T phase of $NaTiSi_2O_6$ all Raman active modes are of the same (A_g) symmetry type. This symmetry change requires the translation symmetry breaking of the TiO_6 chain which is in agreement with pre-

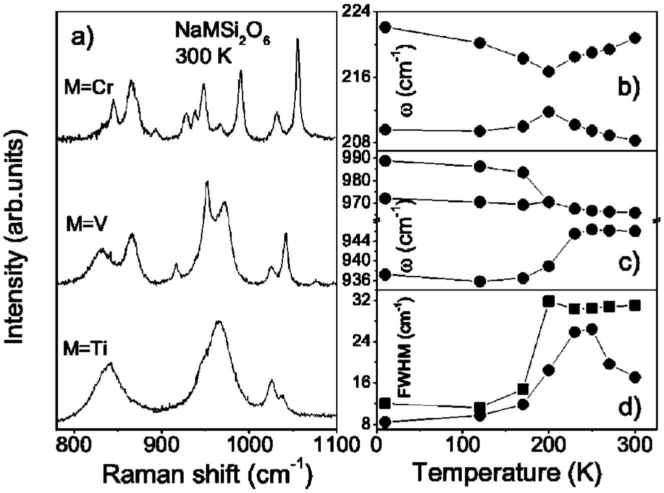

FIG. 3. (a) Raman spectra of $\mathrm{NaMSi_2O_6}$. (b)–(d) Temperature dependence of the phonon frequencies and linewidths in $\mathrm{NaTiSi_2O_6}$.

liminary x-ray diffraction and neutron scattering data.[11] Second, we show in detail the temperature dependence of the structure around 970 $\mathrm{cm^{-1}}$ [Figs. 3(c) and 3(d)]. The mode at about 946 $\mathrm{cm^{-1}}$ softens by about 10 $\mathrm{cm^{-1}}$, while the mode at 966 $\mathrm{cm^{-1}}$ "splits," and hardens by 25 $\mathrm{cm^{-1}}$. The full width at half maximum (FWHM) of the 946 $\mathrm{cm^{-1}}$ (circles) and 966 $\mathrm{cm^{-1}}$ (squares) phonons (the FWHM is estimated from the Lorenzian fit) increases up to the maximum value at about 210 K, and then decreases to the saturation value which is much smaller than the $T=300$ K value, see Fig. 3(d). This means that the bond fluctuations are considerably larger in the high-T phase than in the low-T phase. All phonon anomalies appear at temperature which coincides with the T_c obtained from the susceptibility measurements,[6] indicating that the magnetic ordering is accompanied by a structural phase transition, just as one would expect for a canonical orbital-ordering transition. Due to large phonon broadenings, the high-T Raman spectra can be regarded as effectively consisting of fewer than 30 active modes, as predicted by FGA. From the JT point of view, this means that $\mathrm{TiO_6}$ octahedra are more symmetric than is evident from x-ray structural analysis[10]. In that sense the existence of strong bond fluctuations emphasize the orbital character of disorder in $\mathrm{NaTiSi_2O_6}$ at high T.[13,14] Third, since the largest influence of the structural phase transition is observed for the phonons at energies around 970 $\mathrm{cm^{-1}}$, in Fig. 3(a) we present the comparison between Raman spectra of $\mathrm{NaTiSi_2O_6}$, $\mathrm{NaVSi_2O_6}$, and $\mathrm{NaCrSi_2O_6}$ compounds in this interesting spectral region. The V and Cr-compounds are isostructural with $\mathrm{NaTiSi_2O_6}$ and do not exhibit similar type of phase transition at low temperatures.[6] We find that the phonon line widths dramatically increase in the components with smaller spin values ($V^{3+} \rightarrow S=1$, $Cr^{3+} \rightarrow S=3/2$). As we will discus later on this effect is also a consequence of the orbital dynamics. One should make sure, however, that our experimental observations (in particular the peak broadenings) are not due to spurious effects in the polycrystalline powder samples: grains or secondary phases at the grain boundaries could in principle lead to similar trends in the data. We therefore performed the following checks: (a) the measurements on several different positions (different "grains") on the sample surface produced almost identical spectra, both in high and low temperature phases—we find only a slight difference in a relative intensities of the modes; (b) by using different laser-light energies we obtained the same spectra—we find no resonant effects. Finally, it is hard to believe that such large and sharp phonon shifts at the critical temperature, and the abrupt changes of the phonon broadenings at T_c are just random strain or grain boundary effects.

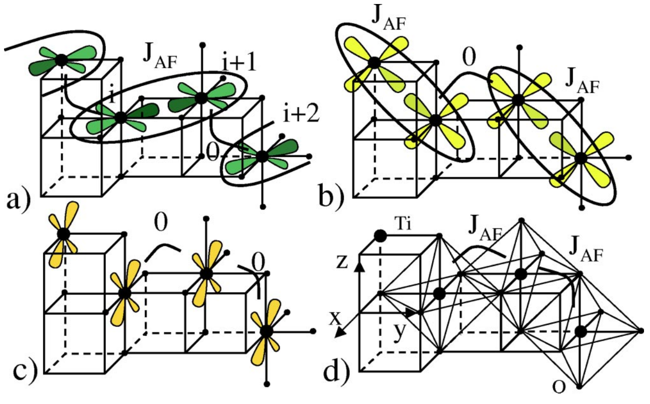

FIG. 4. (Color online) Schematic presentation of the orbital ordering in $\mathrm{NaTiSi_2O_6}$. Orbital overlap in (a) xy, (b) yz, and (c) xz planes. (d) Heisenberg AF phase.

Next we discuss the electronic structure. For the single octahedron the cubic crystal field splits the Ti,V, or Cr $3d$ states into low lying t_{2g} states, with one, two, or three electrons, respectively, and empty states of e_g symmetry at higher energy. The low energy electronic properties are governed by the threefold degenerate t_{2g} states (the relevant states are $|xy\rangle$, $|yz\rangle$ and $|zx\rangle$).[15] The Coulomb interaction U between electrons on the same transition metal atoms is large, so the exchange interactions can be determined by a second order perturbation expansion in the electron hopping parameters. The problem is further reduced by considering the symmetry allowed hopping paths in the chain geometry, schematically represented in Fig. 4. If we consider orbitals on two sites in the same xy plane, then only the hopping between $|xy\rangle$ orbitals is relevant [see Fig. 4(a)]. For sites in the yz plane, the $|yz\rangle$ orbitals are relevant, Fig. 4(b). In the present geometry there are no transition metal atoms in the same chain that are also in the same xz plane. The $|xz\rangle$ orbitals are therefore non-bonding and can be considered inert on this level of approximation (a tightbinding parametrization[16] shows that other overlap integrals either vanish by symmetry or are more than a factor of 5 smaller); see Fig. 4(c). For the $S=1/2$ titanium system we then obtain the Hamiltonian[17]

$$H^{\mathrm{Ti}} = |\mathrm{J}^{\mathrm{Ti}}| \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j \left[\frac{1}{4} + T_i^z T_j^z + \frac{(-1)^i}{2} (T_i^z + T_j^z) \right], \qquad (1)$$

where we use the orbital operators T ($T_i^z = 1/2$ corresponds to an occupied $|xy\rangle$ orbital and $T_i^z = -1/2$ to an occupied $|yz\rangle$

orbital on site i), and i,j are neighboring sites. For the $S=1$ vanadium and $S=3/2$ chromium systems the orbital degree of freedom vanishes ($T=0$) as the both of the *active* orbitals are occupied, so for the spin system we obtain a simple Heisenberg Hamiltonian $H^{\mathrm{V/Cr}}=|\mathrm{J}^{\mathrm{V/Cr}}|\Sigma_{i,j}\mathbf{S}_i\cdot\mathbf{S}_j$. This immediately explains the uniqueness of the Ti ($S=1/2$) system, and the antiferromagnetism in all $S\neq 1/2$ pyroxenes. The ground state of Hamiltonian (1), is clearly a *ferro-orbital* state, with spin-singlets on each bond, where the energy per dimer is $-3\mathrm{J}^{\mathrm{Ti}}/4$. The state with all $|xy\rangle$ occupied is degenerate with the state with all $|yz\rangle$ occupied; see Fig. 4. Those states do differ, however, because the dimerization pattern along the chain is shifted by one lattice spacing. At zero temperature the system is condensed in either one of these two dimerized orbital ordered states and the translation symmetry is spontaneously broken. This explains the structural change at T_c (the alternation of the Ti-Ti distance is a direct consequence of orbital dimerization), the symmetry change and the energy shifts of the phonon excitations in the Raman spectra of $\mathrm{NaTiSi_2O_6}$ and the observation of a large spin gap in the susceptibility measurements.[6]

At high temperatures, due to strong orbital-lattice coupling and the JT effect, the orbital fluctuations produce dramatic effects. Above T_{OO} the static JT distortion disappears: the high-T orbital disordered phase of $\mathrm{NaTiSi_2O_6}$ may be regarded as an orbital fluctuating phase, and on larger time scales the $\mathrm{TiO_6}$ octahedra appear to be undistorted. This causes the crystal to be effectively more symmetric and causes the less-then-expected number of phonon mode effects due to the large broadenings; see Fig. 3(a). In other words, the orbital fluctuations induce large phonon broadenings (the modes with Ti-O bonds in their normal coordinates will be mostly affected—could be around 970 cm^{-1}), as they are indeed found in the high-T Raman spectra of $\mathrm{NaTiSi_2O_6}$. In that respect, the high-T phase of $\mathrm{NaTiSi_2O_6}$ resembles a dynamical JT phase (where the phonon broadening is a signature of the melted static lattice distortions[13,14]). The spin fluctuations above the orbital ordering temperature[6] can be understood within a straightforward mean-field approximation of Hamiltonian (1), where we can decouple orbitals and spins. If the long range order is absent in the orbital sector, we have for the expectation values $\langle T_i^z\rangle=0$, and $|\langle T_i^z T_j^z\rangle|<1/4$, so that the effective exchange constants—and therefore the fluctuations in the spin sector—are still antiferromagnetic. Thus, the nature of the phase transition in $\mathrm{NaTiSi_2O_6}$ can be established: it corresponds to an orbital order-disorder phase transition with appropriate concomitant magnetic and lattice changes. It can also be described as an *orbital analogue of the SP phase transition*. In the case with two electrons per site ($\mathrm{NaVSi_2O_6}$), the orbital fluctuations are strongly suppressed due to the inert property of $|xz\rangle$ orbitals, and the corresponding phonon broadenings are much smaller; see Fig. 3(a). $\mathrm{NaCrSi_2O_6}$ has a fully polarized t_{2g} core, no orbital degrees of freedom, and no anomalous phonon broadenings in the Raman spectra.

We conclude that $\mathrm{NaTiSi_2O_6}$ exhibits an orbital order-disorder phase transition at 210 K. The spin-orbital microscopic model shows that it originates from the instability of the high temperature orbital fluctuating phase, towards a dimerized orbital ordered state, accompanied by a lattice distortion and by spin valence bond formation. We describe the phase transition in $\mathrm{NaTiSi_2O_6}$ as an orbital analogue of the spin-Peierls phase transition.

M.J.K. acknowledges support from the Research Council of the K.U. Leuven and DWTC.

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